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Note

The crystal and molecular structure of 6,8,15,16b,16c,17-hexahydro-16b,16c-diphenyl-7H,16H-6a,7a,15a,16a-tetraazanaphtho[5,6]azulano[2,1,8,-ij]naptho[f]azulene-7,16-dione

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The crystal and molecular structure of a clip containing molecule is described. The structure was solved by vector search methods and refined by least squares methods to $R_1 = 0.0768$ [$I > 2\sigma(I)$]. Crystal data: $C_{40}H_{30}N_4O_2 \cdot HCCl_3$, triclinic, space group $P\bar{1}$, $a = 9.302(2)$, $b = 12.981(2)$, $c = 15.765(2)$Å, $\alpha = 65.91(2)°$, $\beta = 76.40(2)°$, $\gamma = 80.15(1)°$, $V = 1682.9(4)$Å^3, $Z = 2$.

KEY WORDS: Crystal structure; receptor; clip shaped molecule.

Introduction

In the course of our studies aimed at the development of synzymes (synthetic enzymes),[1a,1b] a new series of clip shaped molecules were designed in order to get a better insight into the factors which influence the binding of dihydroxybenzene molecules into these receptors.[2] From earlier studies[3] it is known that clip molecules with 1,4 dimethoxynaphtalene (**1a**) or functionalized 1,4 dimethoxybenzene side walls (**2**)[4] are not able to bind aromatic guest molecules. A possible explanation is that the methoxy groups are blocking the carbonyl groups of the diphenylglycoluril. Therefore, we synthesized a clip molecule with napthalene moieties (2,3 connected) not having the methoxy groups (**1b**), in order to study the role of these groups. An X-ray diffraction experiment was undertaken to establish the three-dimensional structure of the compound synthesized. The structure appeared to be the title compound.

Experimental

The crystal data and a summary of the data collection, the structure solution and refinement are given in Table 1. The atomic positional and vibrational parameters are given in Table 2. Since experience showed that the diphenylglycoluril unit from similar compounds can be used as a suitable rigid fragment[6] for structure solution, this unit was input to a vector search program.[7] The phasing power of the model proved to be sufficient to solve the stucture. The hydrogen atoms of the methyl groups were obtained by rotation of an idealized methyl group to match maximum electron density in a difference Fourier synthesis. The remaining hydrogens were generated at calculated positions. All hydrogens atoms were refined riding on the parent atoms with constrained isotropic temperature factors. A difference Fourier synthesis revealed the presence of one chloroform solvent molecule which is partly disordered. One of the chlorine atoms of the

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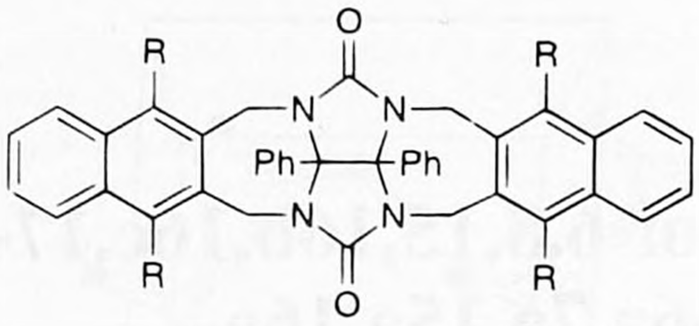
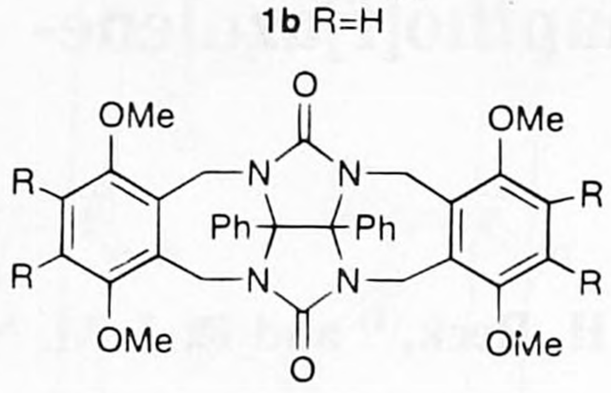


1a R=OMe
1b R=H



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Scheme 1

chloroform molecule was split into two parts. The corresponding occupation factors were set to add up to one during refinement.

Discussion

The structure and atomic numbering are presented in Fig. 1.[11] Geometrical calculations[12] revealed no unusual geometrical features. Calculations with PLATON[13] revealed no higher symmetry and no further residual solvent accessible area. There is a hydrogen bond between the hydrogen atom of the chloroform molecule and the carbonyl oxygen of the diphenylglycoluril unit (O–H: 2.18(4) Å; / O–H–C: 172.(3)°). Comparing the structures of **1a** and **1b** one can conclude that the cavities of these clip shaped molecules are very similar. There are some differences like the

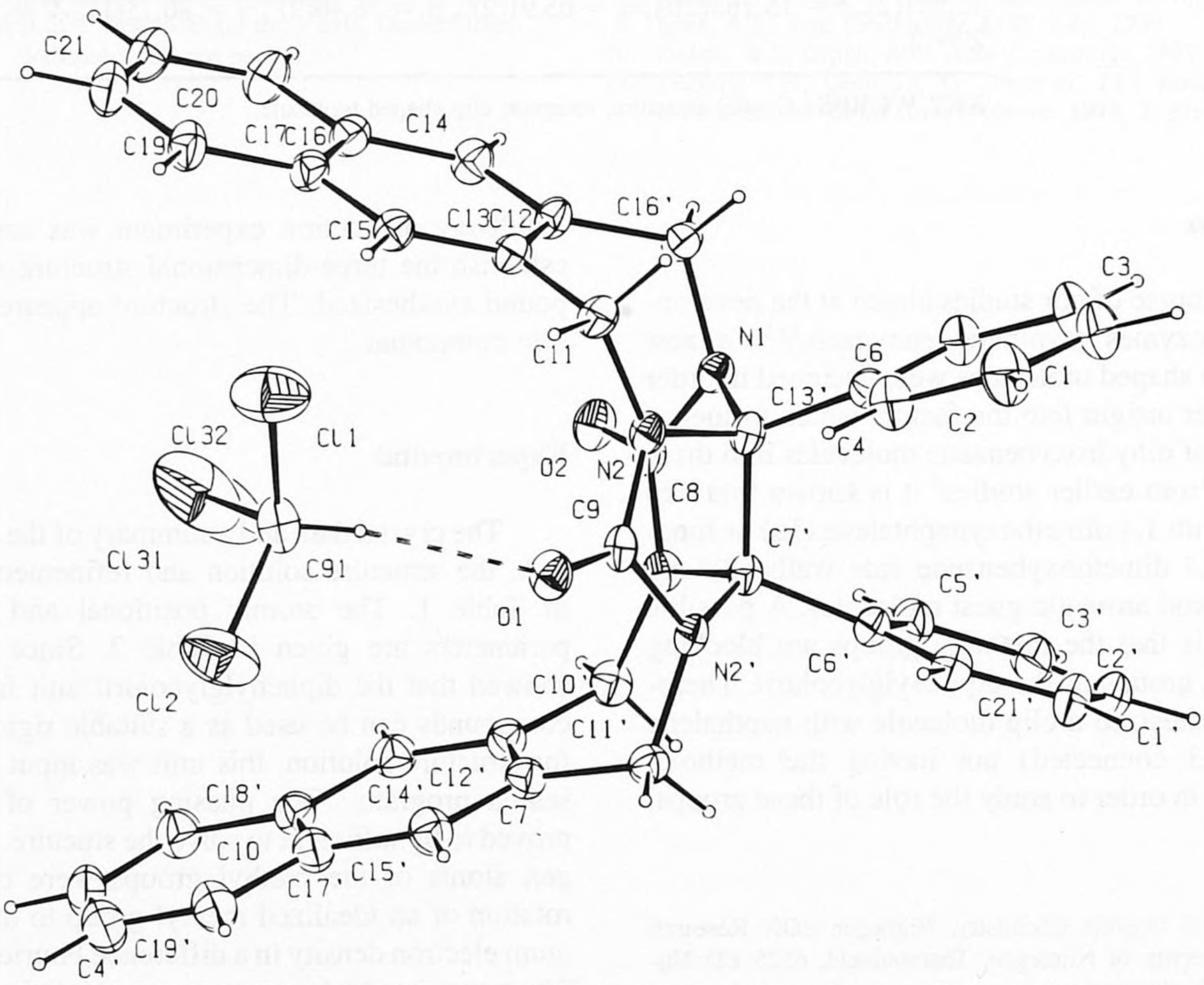

Fig. 1. ORTEP drawing with atomic numbering. Thermal ellipsoids are at 40% probability.

Table 1. Crystal data and summary of intensity data collection, structure solution, and refinement

Crystal data	
Compound	$C_{40}H_{30}N_4O_2 \cdot HCCl_3$
Color/shape	Colorless/regular
Crystallization	Chloroform
Formula weight	718.05
Crystal system	Triclinic
Space group	$P\bar{1}$
Temperature, K	208(2)
Cell constants[a]	
a, Å	9.302(2)
b, Å	12.981(2)
c, Å	15.765(2)
α, °	65.92(2)
β, °	76.40(2)
γ, °	80.15(1)
Cell volume, Å^3	1682.9(4)
Formula units/unit cell	2
D_{calc}, g cm^{-3}	1.417
μ_{calc}, mm^{-1}	0.317
F(000), electrons	744
Intensity data collection	
Diffractometer/scan	Enraf-Nonius CAD-4/ω-scan
Radiation, graphite monochromator	Mo*K*α (λ = 0.71073 Å)
Crystal dimensions, mm	0.09 × 0.13 × 0.39
Scan width, °	1.5
Standard reflections	3, every 7200 seconds exposure time
Decay of standards	1.00–1.02
Reflections measured	16212
2θ-range °	up to 56
Range of *h*, *k*, *l*	$-12 \le h \le 12$, $-17 \le k \le 17$, $-20 \le l \le 20$
Corrections	
Lorenz-polarization	
EMPABS[5] correction	0.993–1.011
Independent reflcns (obs., $I_o > 2\sigma(I_o)$)	8106(4210)
R_{merge}[b]	0.063
Computer programs[c]	Local programs
Structure solution and refinement	
Structure solution	Vector search methods[7]
Computer programs	DIRDIF[8] (ORIENT, TRACOR)
Structure refinement	Full-matrix, least-squares on F^2
non-H atoms	Anisotropic
H-atoms	See experimental
Computer programs	SHELXL[9]
Shift/esd	Less than 0.04
No. of restraints/parameters	0/464
Goodness-of-fit on F^2	1.005
R indices [I > 2σ(I)]	$R_1 = 0.059$, $wR_2 = 0.122$
R indices (all data)	$R_1 = 0.139$, $wR_2 = 0.156$
Largest diff. peak and hole, e·Å^{-3}	0.648 and −0.503

[a] Least-squares refinement for 25 reflections, $9.5° < \theta < 13°$.
[b] $R_{merge} = \Sigma\|F_o| - \langle|F_o|\rangle/\Sigma|F_o|$.
[c] Using neutral scattering factors and anomalous dispersion corrections.[10]

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}
O(1)	4945(2)	3638(2)	1730(1)	33(1)
O(2)	−735(2)	4113(2)	3906(1)	32(1)
N(1)	1518(2)	4633(2)	3926(2)	23(1)
N(2)	3760(3)	4025(2)	3043(2)	24(1)
N(1′)	869(3)	5062(2)	2539(2)	25(1)
N(2′)	3354(3)	5245(2)	1623(2)	23(1)
C(1)	5370(4)	7141(3)	3671(3)	48(1)
C(2)	6062(4)	6466(3)	3180(3)	47(1)
C(3)	3893(4)	7058(3)	4066(3)	47(1)
C(4)	5269(4)	5735(3)	3071(2)	35(1)
C(5)	3089(4)	6325(3)	3965(2)	34(1)
C(6)	3762(3)	5672(2)	3448(2)	25(1)
C(7)	2857(3)	4976(2)	3234(2)	24(1)
C(8)	418(3)	4544(2)	3497(2)	24(1)
C(9)	4100(3)	4222(2)	2106(2)	25(1)
C(10)	1632(3)	3816(2)	4881(2)	27(1)
C(11)	4387(3)	3071(2)	3783(2)	28(1)
C(12)	1943(3)	2606(2)	4959(2)	26(1)
C(13)	3257(3)	2241(2)	4437(2)	26(1)
C(14)	941(3)	1832(3)	5542(2)	29(1)
C(15)	3499(3)	1137(2)	4531(2)	26(1)
C(16)	1173(3)	684(3)	5653(2)	28(1)
C(17)	2479(3)	324(2)	5141(2)	27(1)
C(18)	148(4)	−115(3)	6254(2)	37(1)
C(19)	2718(4)	−818(3)	5244(2)	33(1)
C(20)	410(4)	−1214(3)	6337(2)	39(1)
C(21)	1700(4)	−1574(3)	5834(2)	39(1)
C(1′)	1597(5)	9179(3)	1626(2)	46(1)
C(2′)	2974(5)	8698(3)	1328(2)	44(1)
C(3′)	435(4)	8526(3)	2090(2)	42(1)
C(4′)	3142(4)	7548(3)	1500(2)	34(1)
C(5′)	613(4)	7368(3)	2285(2)	33(1)
C(6′)	1979(3)	6875(2)	1992(2)	26(1)
C(7′)	2239(3)	5598(2)	2290(2)	23(1)
C(10′)	−20(3)	5190(3)	1849(2)	29(1)
C(11′)	3013(3)	5451(3)	699(2)	27(1)
C(12′)	615(3)	4462(2)	1281(2)	27(1)
C(13′)	2079(3)	4591(3)	726(2)	27(1)
C(14′)	−226(3)	3699(3)	1273(2)	31(1)
C(15′)	2617(4)	3947(3)	198(2)	33(1)
C(16′)	319(4)	3037(3)	713(2)	31(1)
C(17′)	1770(3)	3156(3)	175(2)	32(1)
C(18′)	−555(4)	2267(3)	679(2)	38(1)
C(19′)	2314(4)	2492(3)	−382(2)	38(1)
C(20′)	−6(4)	1664(3)	116(3)	41(1)
C(21′)	1434(4)	1767(3)	−406(3)	42(1)
Chloroform molecule (Occupation factors for the disordered Cl(31) and Cl(32) : 0.50(5))				
C(91)	5260(4)	1138(3)	1964(3)	41(1)
Cl(1)	6549(1)	390(1)	2701(1)	70(1)
Cl(2)	5869(1)	1102(1)	845(1)	75(1)
Cl(31)	3502(11)	736(15)	2423(10)	101(3)
Cl(32)	3579(12)	539(16)	2488(10)	111(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

tapering of the cavities and the twist in the molecules. These differences are, however, a result of crystal packing effects and are consistent with the flexibility of the molecules. From binding studies we concluded that clip **1b** is indeed able to bind 1,3 dihydroxy benzene, however, with a low association constant (60 M^{-1}). These data suggest that the methoxy groups of **1a** are indeed playing an important role in blocking the cavity for the binding of aromatic substrates, although, other effects are likely to be involved as well. Further studies to confirm this hypothesis will be reported elsewhere.

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